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Quantification of trace elements in surgical and KN95 face masks widely used during the SARS-COVID-19 pandemic

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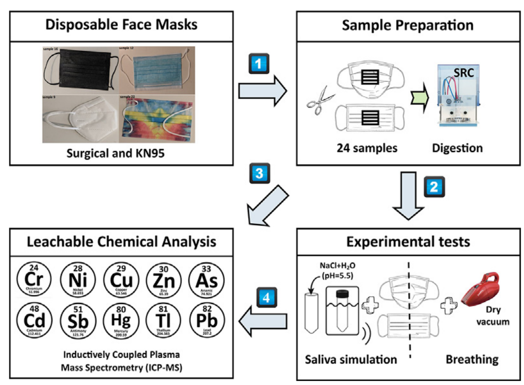
HIGHLIGHTS

- Detection of trace metals and metalloids in 24 disposable face masks
- Monitoring and analysis of 12 (on total) trace elements by ICP-MS
- Leaching of trace metal(loid)s in breathing and saliva simulation experiments
- Leachable concentrations of lead, copper, zinc and antimony were detected.

GRAPHICAL ABSTRACT



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ABSTRACT

During the current coronavirus disease (COVID-19) pandemic, face masks have been the single most important protective equipment against the threat of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2). While masks are worn, both the nose and the mouth of the user come in contact with the mask material, and as the latter mediates the inhaled air and may interfere with the swallowed saliva, it is of paramount importance to assure that the mask is free of toxic substances. As there are currently no studies on the total amount of trace elements in masks, the present study fills the void and investigates 24 surgical and KN95 face masks. Specifically, mask samples were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the total concentrations of trace elements as well as to assess the possibility that any detected of the elements present could transfer into the human body, based on saliva leaching and breathing experiments. Accordingly, it is reported herein that although most masks analyzed in this study contain trace elements below their corresponding detection limits, a few masks did contain detectable levels of trace elements. In particular, the maximum values that were determined in certain analyzed samples were: Pb (13.33 μg g^{-1}), Cu (410 μg g^{-1}), Zn (56.80 μg g^{-1}), and Sb (90.18 μg g^{-1}). Finally, in the masks that Pb was present, it easily leached out (58% transfer during a 6-h exposure) during the saliva simulation experiments.

1. Introduction

The ongoing COVID-19 pandemic has resulted in an unprecedented loss of human life as well as serious post-disease implications to people all around the world regardless of age, living place, health status, or

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other distinguishing parameters (Arolas et al., 2021; Nalbandian et al., 2021). Moreover, the social life of people at all levels has been severely disrupted, especially by the dramatic restrictions regarding social conduct advised by health authorities and mandated by governments (Giuntella et al., 2021). Accordingly, healthcare authorities worldwide, such as the Centers for Disease Control and Prevention (C.D.C.) in the U.S., have introduced two practical and easy to implement measures for facilitating social conduct; the practice of wearing face masks and maintaining six feet (≈2 m) social distancing. Although the latter guideline does not necessitate the use of any medium, the former requires the use of a face mask, which is made of a material (raw/virgin or recyclable) of a certain chemical composition, manufactured by the chemical industry. As there have been scientific reports of toxic substances, including highly toxic elements, such as Pb, found in products made of materials similar to those of masks, there is a critical need for testing and monitoring of toxic substances on the highly used face masks to ascertain safety (Turner and Filella, 2021; Ferg and Rust, 2007; Filella et al., 2020).

In particular, both surgical and KN95 masks, are composed of synthetic thermoplastic carbon polymers, such as polypropylene (PP), polyurethane (PU), polyacrylonitrile (PAN), polystyrene (PS), polycarbonate (PC), polyethylene (PE), or polyester (PES) (Armentano et al., 2021), which are synthesized by a variety of chemical processes (Pu et al., 2018). These require a range of heavy metal and metalloid catalysts, which include: Sb in the form of oxides and acetates (PES, PE, PP, PS, PES, PAN), Ti and Zr compounds (PP, PS, PE), Sn complexes (PU) and several other metal-containing compounds (Kaminsky and Fernandez, 2008; Filella, 2020; Scott, 2005). In addition, to the catalytic function, heavy metals and metalloids are involved in several other stages of polymer manufacturing such as: additives for flame retardants (Sb and Al oxides) (Yurddaskal et al., 2018), pigments (Pb, Cd, Cr, and Cu compounds) (Wheeler, 1999), and stabilizers (Pb and Cd compounds) (Grossman and Krausnick, 1997). Finally, Cu nanoparticles incorporated into polymer matrices are used to develop polymer nanocomposites with antibacterial properties (Palza, 2015). Overall, the most common trace metal(loid) s detected in carbon polymers are Cu, Zn, Pb, Cd, Cr, Mo, Sn, Sb, and Co (Munier and Bendell, 2018; Whitt et al., 2016; Özer et al., 2011).

Masks come in contact with the face, and in particular the nose and mouth of the wearer, but also mediate the inhaled air, and thus there is always the possibility of a toxic substance present impacting the mask user. Consistent with this, there are recent studies in the literature regarding masks containing microplastics (Aragaw, 2020a; Li et al., 2021). The same is true when a mask comes in contact with the swallowed saliva of the wearer, especially while talking, or when worn by a child. Several factors can compound such exposure, including the need of wearing masks for extended periods of time (e.g. during a full workday), as well as the use of masks by people of all ages, including children, and the usage of masks in a variety of settings such as homes, offices, restaurants, places of worship, schools, etc. (Yu et al., 2021).

In addition to the possibility of health hazards from contaminants contained in face masks, there can also exist considerable environmental hazards, which are magnified by the current unprecedented pace of production, use, and disposal of face masks in the midst of the pandemic (Aragaw, 2020b). Accordingly, the continuous monitoring, testing, and reporting of pollutants, including heavy metals and metalloids in commercially available face masks is a matter of paramount importance.

With the purpose of addressing the importance of testing face masks for trace elements, the total concentration of 12 trace elements (Cu, Pb, As, Cd, Sb, Hg, Zn, Ni, Cr, Tl, Se, Mn) was first assessed, in 24 highly used, surgical and KN95 mask samples, using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Secondly, a saliva leaching simulation as well as a breathing experiment were conducted to assess the transfer of trace elements into the human body. The 24 analyzed mask samples included several of the bestselling brands available on the online marketplace, masks sold by retail stores, masks of different colors, and finally, masks for children. The trace elemental analysis results from the total digestion of this work were compared with the results of a metal leachate from a recently reported study (Sullivan et al., 2021). Finally, the ICP-MS analysis was conducted using the appropriate reference standard. Overall, the aim of the present study was to examine the presence of trace elements after total acid digestion of face masks, as well as to examine how trace metals may transfer out of the masks.

2. Experimental

2.1. Materials and methods

A total of 24 face mask samples (Table 1) were selected and purchased mainly from the online marketplace, considering that this is one of the primary sources of mask products during the pandemic. The selection included mostly surgical masks as these have been the most common type of masks worn by the public, as well as three samples of KN95 masks. The latter have been the practical substitute for N95 masks, which are mostly unavailable to the public due to their heavy use by health care professionals. Samples included mostly the typical blue masks, several black-colored masks, and two multicolor masks. Finally, while most of the samples were adult size, we also included two children size masks. When the purchases were made (11/20/2020, 2/27/2021, 3/15/2021, and 4/2/2021) several masks were listed as “Amazon's choice”, “#1 Amazon Best Seller”, or had the largest number of “Amazon ratings”.

For example, samples #1 and #2, have been among the bestselling KN95 masks on Amazon, with #2 having more than 15,000 “Amazon ratings”. Samples #3, #4, #5 have been among the bestselling surgical masks on Amazon, with #3 having more than 52,000 Amazon ratings. Sample #10 has been among the bestselling “Black Disposable Face Masks” on Amazon with more than 95,000 “Amazon ratings”. Sample #11 was the “#1 Amazon Best Seller” in “Surgical masks” at the time of the purchase. Sample #22 was the “Amazon's Choice” in “Medical Masks for kids”. Other retailers used include Walmart (2 samples), Dollar Tree (2 samples), Fischer Scientific (1 sample) and Raindew (4 samples). Pictures of selected samples are shown in Fig. 1.

2.2. Determination of trace elements

2.2.1. Sample preparation

The masks were cut into strips (metal structures and elastics were removed and the center part was analyzed). Next 0.25 g of each sample

Table 1
Main characteristics of the investigated face mask samples.

Mask sample ID	Type	Color	Size	Purchased from	Purchase date
1	KN95	White	Adult	Amazon.com	11/20/2020
2	KN95	White	Adult	Amazon.com	11/20/2020
4	Surgical	Blue	Adult	Amazon.com	11/20/2020
5	Surgical	Blue	Adult	Dollar Tree	11/20/2020
6	Surgical	Blue	Adult	Amazon.com	2/27/2021
7	Surgical	Blue	Adult	Amazon.com	2/27/2021
8	Surgical	Blue	Adult	Amazon.com	2/27/2021
9	KN95	White	Adult	Amazon.com	2/27/2021
10	Surgical	Black	Adult	Amazon.com	3/31/2021
11	Surgical	Blue	Adult	Amazon.com	2/27/2021
12	Surgical	Blue	Adult	Dollar Tree	3/15/2021
13	Surgical	Blue	Adult	Amazon.com	3/15/2021
14	Surgical	Blue	Adult	Fischer Sc.	12/1/2020
15	Surgical	Blue	Adult	Raindew	3/31/2021
16	Surgical	Black	Adult	Raindew	3/31/2021
17	Surgical	Blue	Adult	Walmart	3/31/2021
18	Surgical	Blue	Adult	Walmart	3/20/2021
19	Surgical	Black	Adult	Amazon.com	4/2/2021
20	Surgical	Black	Adult	Amazon.com	4/2/2021
21	Surgical	Black	Kids	Amazon.com	4/2/2021
22	Surgical	Multicolor	Kids	Amazon.com	4/2/2021
23	Surgical	Black	Adult	Raindew	4/2/2021
24	Surgical	Multicolor	Adult	Raindew	4/2/2021

Fig. 1. Photos of selected face masks after taken out of their package.

was weighed in a 15 mL quartz digestion vessel. 5 mL of concentrated HNO_3 (double distilled, prepared onsite) and 2 mL of high purity deionized water, (resistivity 18.2 MΩ-cm) were added to each vessel. The samples were then digested in an Ultrawave single reaction chamber (SRC) microwave digestor (Milestone, Shelton, CT). The microwave program was as follows: 30-min ramp to 230 °C, after which the temperature was held for an additional 10 min, and then the samples were allowed to cool below 30 °C. The samples were then diluted to 50 mL with de-ionized (>18.2 MΩ) water. A reagent blank and a 0.25 g aliquot of Certified Reference material ERM®-EC680m (European Commission Joint Research Centre Institute for Reference Materials and Measurements, Geel, Belgium) (trace elements in low-density polyethylene) were also digested with each batch to monitor accuracy. Three aliquots of each mask were prepared and analyzed to test the reproducibility among the masks.

2.2.2. Instrument - measurements

The samples were analyzed on an Agilent 7900 ICP-MS system (Agilent Technologies, Santa Clara, CA), equipped with MassHunter Software and an Agilent Technologies SPS 4 autosampler. A quartz concentric nebulizer, spray chamber and torch were used. The typical operating conditions are listed in Table S1 (in Supplementary material). The instrument performance was checked before each run using a solution consisting of 1 μg L^{-1} each of Li, Co, Y, Ce, and Tl in 1% HNO_3. Typical ion counts were 50,000 s^{-1}, 250,000 s^{-1}, and 160,000 s^{-1} for Li, Y, and Tl, respectively, with relative standard deviations between 1.5% and 3.2%. The doubly charged ion ratio ($^{140}Ce^{2+}/^{140}Ce^{+}$) and oxide ratio ($[^{140}Ce^{16}O]^{+}/^{140}Ce^{+}$) were maintained below 3%. The sample solution and the internal standard solution (consisting of 500 mg L^{-1} of Sc, Y, In, Tb, Ir and Bi) were pumped by a peristaltic pump and mixed in a mixing block before being introduced into the nebulizer. Masks #1–18 were analyzed for the following elements: Cr, Ni, Cu, As, Cd, Sb, Hg, Tl, and Pb, as a preliminary test. Subsequently, masks #19–24 were analyzed for Cr, Mn, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, and Pb and three replicates per sample were analyzed. Pb concentrations were obtained by summing the ion counts for ^{206}Pb, ^{207}Pb, and ^{208}Pb. During the sample analysis, three points per mass were sampled for each element, with an integration time of 0.1 s per point for all elements except As, Se, and Cd for which an integration time of 0.9 s per point was used, and Pb, for which an integration time of 0.5 s for each isotope was used. The calibration range was 0–25 ng g^{-1} for all elements except Zn, where the calibration range was from 0 to 250 ng g^{-1}. The linear dynamic range was verified to 1000 ng g^{-1} for Zn and 100 ng g^{-1} for the other elements. The linear regression statistics were above 0.998 for all elements. A 10 ng g^{-1} continuing calibration verification (CCV) was analyzed every 10 samples for Cr, Ni, Cu, As, Cd, Tl and Pb and at 1 ng g^{-1} CCV was used for Hg. All CCVs were within ±10%. The octopole reaction cell was used in collision mode with energy discrimination in-order to reduce polyatomic interferences that are generated in the plasma. Mean values for ERM®-EC680m were within ±10% of certified values, except Sb which were within ±40%. The relatively low recovery of Sb was consistent throughout the runs. Sb has an extreme tendency to hydrolyze (it possibly forms poorly soluble antimony ions such as SbO^{+} even in concentrated acids). In acids, these also form volatile antimony salts. At slightly acidic pH it precipitates as antimony hydroxide (Zheng et al., 2001). Spike recoveries for all elements were from 80 to 103%, except for Sb, which was 70%, consistent with the CRM recovery. The detection limits for all the elements analyzed in this study are listed in Table S2 (in Supplementary material).

2.3. Breathing experiment

Mask samples #19–24 were used for the breathing experiment. The inside part of the masks was subjected to vacuum for 15 min using a commercially available vacuum device (Dirt Devil Scorpion, model SD20005REDSD20005RED). Although this experiment does not mimic breathing, the process of vacuuming a mask in essence constitutes the forcing of large amounts of air through the mask material. This can relate to the way that upon breathing, air is pushed through the mask material by the breathing process of the mask user. As a result, if a contaminant in the mask is transferable, it will be a contaminant that passes through in the vacuuming experiment, and in an analogous manner, a contaminant may transfer through during the breathing process of the mask user. This experiment was conducted to observe the potential release of trace elements from masks. Upon vacuuming, the samples were analyzed by ICP-MS in triplicates to determine any change of elemental concentrations.

2.4. Saliva simulation

Mask samples #19–24 were used for the saliva simulation as part of the second run of ICP-MS analysis, following the preliminary first run, which focused on the detection of elements. A part of the mask was extracted in saline solution to evaluate the migration of trace elements when exposed to saliva. Fragments of the mask tissue (central part of the mask) weighing 0.5 g were placed in 50 mL polypropylene centrifuge tubes, and 25 mL of a 0.9% saline solution (chemical composition: NaCl, H_2O, and pH = 5.5) were added. The samples were then immersed in a heated shaker bath with the temperature set to 37.5 °C (as this relates to the circadian cycle of a person's body temperature) for 6 h. The resulting extracts were then acidified to ≈1% HNO_3 and analyzed via ICP-MS as it is referenced above.

3. Results and discussion

Considering the implications of trace elements in the chemical manufacturing of the mask polymeric material, the possibility of heavy metals and metalloids being present in commercially available face masks was initially examined, with the aim to record for the first-time their total concentrations. While the present study is the first attempt to measure total concentrations after a complete digestion, a recently published study by Sullivan et al., examined the findings of heavy metals in water leachates from face masks (Sullivan et al., 2021).

ICP-MS was chosen for trace elemental analysis as this technique is a well-established method for the detection of trace elements at concentrations of ng g^{-1} and even as low as pg g^{-1}. The low detection limits have established ICP-MS as the method of choice for trace elemental analysis in the medical and forensic science fields (Reidy et al., 2013).

The attention was initially focused on nine highly toxic heavy metals and metalloids (Cr, Ni, Cu, As, Cd, Sb, Hg, Tl and Pb). Analysis showed concentrations below the detection limit for six elements (Cr, Ni, As, Cd, Hg, and Tl), however there were observed detectable concentration levels for Cu, Sb and Pb (Table 2).

Specifically, Cu was detected in most of the surgical masks (18 out of 24 samples) in the range of 2.24 to 410 μg g^{-1}, while Cu was not detected in all three analyzed KN95 masks (samples #1, 2, and 9), the highest Cu value was measured in sample #6 (410 μg g^{-1}). Sb was detected in 10 out 24 samples, both surgical and KN95 masks, with a range of 0.97 to 90.18 μg g^{-1}. Noticeably, the mask with the second highest amount of Sb (86.53 μg g^{-1}) was a children's mask (sample #22). Among the largest concentrations of Sb were those measured in samples #1 and #2 which were of the KN95 type. Pb was detected in 14 out of 24 mask samples, in both surgical and KN95 masks, and ranged from 0.15 to 13.33 μg g^{-1}. Noticeably, Pb was detected in 3 out of 4 black colored masks (samples #16, 19, 20, and 23), with the highest concentration found for sample #16 at 13.33 μg g^{-1} (Fig. 2).

Table 2
Mask Sample concentrations in (μg g^{-1}).

Mask sample ID	Cr	Ni	Cu	Zn	As	Cd	Sb	Hg	Tl	Pb
1	N.D.	N.D.	N.D.	N.A.	N.D.	N.D.	81.50	N.D.	N.D.	0.51
2	N.D.	N.D.	N.D.	N.A.	N.D.	N.D.	90.18	N.D.	N.D.	N.D.
3	N.D.	N.D.	93.1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	0.49
4	N.D.	N.D.	120	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	1.37
5	N.D.	N.D.	134	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
6	N.D.	N.D.	410	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	0.66
7	N.D.	N.D.	107	N.A.	N.D.	N.D.	2.21	N.D.	N.D.	N.D.
8	N.D.	N.D.	169	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	0.48
9	N.D.	N.D.	N.D.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
10	N.D.	N.D.	38.7	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	1.70
11	N.D.	N.D.	123	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	0.62
12	N.D.	N.D.	206	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	0.77
13	N.D.	N.D.	183	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
14	N.D.	N.D.	313	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	0.69
15	N.D.	N.D.	165	N.A.	N.D.	N.D.	3.15	N.D.	N.D.	N.D.
16	N.D.	N.D.	31.9	N.A.	N.D.	N.D.	10.47	N.D.	N.D.	13.33
17	N.D.	N.D.	126	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
18	N.D.	N.D.	338	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
19	N.D.	N.D.	5.50	30.10	N.D.	N.D.	4.53	N.D.	N.D.	0.15
20	N.D.	N.D.	2.24	15.93	N.D.	N.D.	7.15	N.D.	N.D.	1.50
21	N.D.	N.D.	N.D.	23.09	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
22	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	86.53	N.D.	N.D.	N.D.
23	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.83	N.D.	N.D.	0.37
24	N.D.	N.D.	3.18	56.80	N.D.	N.D.	0.97	N.D.	N.D.	1.38

N.D. = Not Detected, N.A. = Not Analyzed.

The significance and alarming levels of the measured values become evident upon reviewing the inhalation and oral toxicity (the two possible exposure routes related to a mask use) of Zn, Cu, Pb and Sb. Specifically, upon inhalation, Sb in amounts greater than 8.87 mg m^{-3}, can cause pneumoconiosis, while other respiratory effects recorded are chronic bronchitis, chronic emphysema, inactive tuberculosis, pleural adhesions, and respiratory irritation (Sundar and Chakravarty, 2010). For ingestion (drinking water), the safe limit set by the U.S. Food and Drug Administration (FDA) is 0.006 mg L^{-1} (Sundar and Chakravarty, 2010). Additionally, it is noteworthy that Sb in the form of oxide (which is used in the synthesis of the polymer mask material) is classified as a possible carcinogen for humans. Comparing these values to our measured range of Sb (0.97 to 90.18 μg g^{-1}), an extremely high level of the element in mask sample #2 was measured. Extraordinarily, the list of face masks containing Pb (sample #22) includes a commercially available bestselling children's mask.

Inhaled and ingested Pb can cause severe brain damage, reproductive system damage and death (Cleveland et al., 2008). The toxicity of Pb is probably among the most well-studied as thousands of people are poisoned every year upon inhalation and oral exposure. Upon inhalation, Pb is deposited in the lungs, where 95% of it enters the bloodstream and 15% of the ingested Pb is absorbed (Kumar et al., 2020). The Occupational Safety and Health Administration (OSHA) under the United States Department of Labor set a permissible exposure limit of Pb to no greater than 50 μg m^{-3} averaged over an 8-h period, while the C.D.C. in the U.S. sets the case definition for elevated blood Pb the reference value of 5 μg L^{-1}, which identifies adults and children with elevated levels of Pb (CDC, 2021; 1910.1025 - Lead. | Occupational Safety and Health Administration, (https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1025 (accessed May 22, 2021).

Samples #19, 20, 21, and 24 had measurable amounts of Zn ranging from 15.93 to 56.80 μg g^{-1} (Table 2). Zn is an essential trace element required for the maintenance of health. However, an excess of it can cause lethargy and respiratory tract problems such as metal fume fever (MFF). Excessive levels of Zn (300–600 μM for 15 min.) have been reported to result in extensive neuronal death in cortical cell culture (Plum et al., 2010; Yokoyama et al., 1986). Additionally, most masks analyzed (18 out of 24 samples) contained considerable amount of Cu ranging from 2.24 (sample #20) to 410 μg g^{-1} (sample #6). Cu is also an essential trace element with many roles in the human body, but it is known to produce toxic effects to humans as well as to the environment (Leal et al., 2018).

The environmental impact of heavy metals and metalloids contained in face masks is also significant as the production, usage, and disposal of face masks during the pandemic has reached unprecedented levels (Aragaw, 2020a). Heavy metals and metalloids in masks may eventually find their way into the oceans. In a study about microplastics in oceans in Vancouver, British Columbia, Munier et al. found that such microplastics had the ability to either sorb or desorb Zn, Cu, Cd and Pb from manufactured polymers (Munier and Bendell, 2018). Confirming this, Ashton *et. al* reported enrichment of Cd and Pb in manufactured pellets sampled from four beaches along a stretch of coastline in south Devon, SW England (Ashton et al., 2010). Once metal(loid)s in plastics end up in oceans, they are usually ingested by fish and work their way up the food chain in humans (Lusher et al., 2020; Chan et al., 2019; Neves et al., 2015).

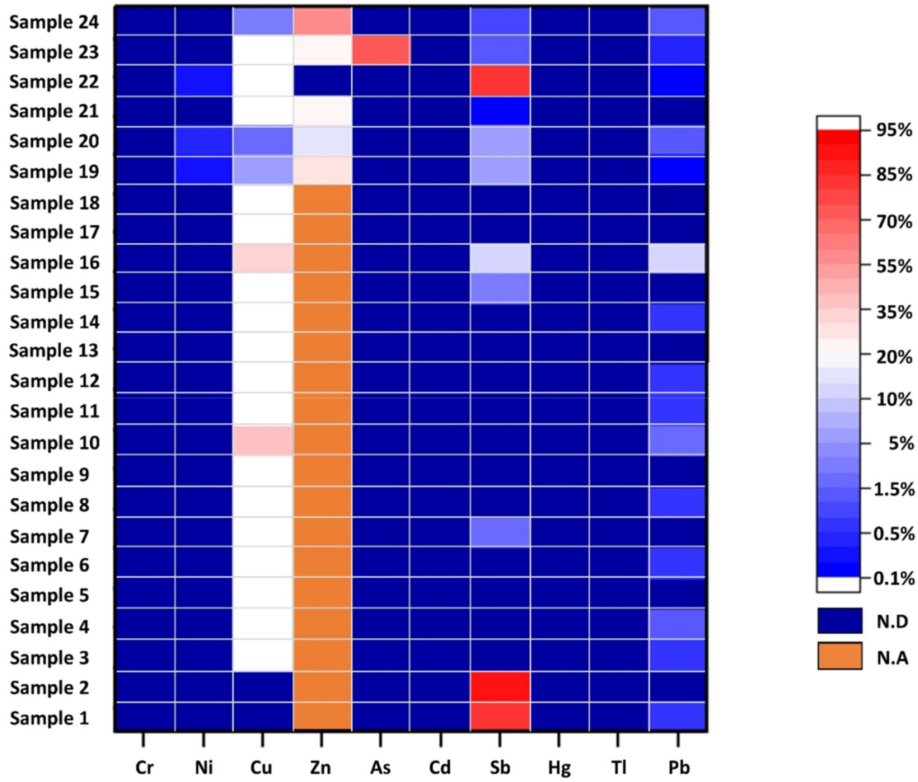

Fig. 2. Heatmap representation of heavy metal(loid)s identified in the 24 face mask samples. Red color represents high concentrations and blue color indicate low contents of heavy metal (loid)s regarding their probability of occurrence (up to 95%).

As detectable amounts of trace metals were obtained in the first set of our analysis, this was followed by a second analysis of selected masks (samples #19–24) using ICP-MS (Table 3). These samples were selected because they represent masks with characteristics relating to the highest concentrations of heavy metals and metalloids measured. The samples included primarily surgical masks, of black color, and/or of multicolor (not of the typical blue color). ICP-MS analysis for different masks of the same brand was carried out and the average concentrations and standard deviations for the amounts of the detected elements are reported. The analysis revealed the important fact that different masks of the same brand, in the same box, were found to contain different concentrations of metals. This is an observation that has been reported before (Sullivan et al., 2021), and it can be attributed to a lack of quality control by the manufacturer. Zn was found in the range of 15.93 to 56.80 μg g^{-1} (samples #19, 20, 21, 24), with the upper value recorded for sample #24. Although Zn is relatively nontoxic taken orally, it has been reported to be toxic upon inhalation (Leal et al., 2018).

Additionally, the potential transfer of trace elements was evaluated by a breathing experiment as trace elements could be inhaled by the mask wearer through either the oral and/or nasal cavities as the typical mask user usually wears a mask for long periods of time. Using mask samples #19–24, a vacuuming experiment was conducted in which masks were vacuumed using a high vacuum applied to the inside, center part, of the mask. As it is evident from the recorded values (Table 3), this did not result in a significant decrease of the measured trace element concentrations as all values were within $\pm 2\sigma$.

In a final experiment, mask samples #19–24 were subjected to a saline leaching simulation using saline water, which is a medium closely mimicking saliva. Specifically, both vacuumed and unvacuumed masks were immersed in saline water of concentration 0.9% for 6 h before ICP-MS analysis was run. As it is indicated in Table 4, no transfer of Zn to the leachate was observed for any of the masks. However, there were detectable levels of Sb from the leachate in both masks of samples #22 and #23. For the two masks for sample #22, the Sb transferred to the leachate was 1% for the non-vacuumed and 2% for the vacuumed,

Table 3
Mask sample concentrations in (μg g^{-1}) measured in vacuuming experiments.

Mask Sample	Cr	Mn	Ni	Cu	Zn	As	Se	Mo	Cd	Sb	Tl	Pb
19 N.V.	N.D.	N.D.	N.D.	5.50 ± 0.88	30.10 ± 3.92	N.D.	N.D.	N.D.	N.D.	4.53 ± 5.16	N.D.	0.15 ± 0.02
19 V.	N.D.	N.D.	N.D.	4.77 ± 0.36	26.36 ± 2.38	N.D.	N.D.	N.D.	N.D.	5.16 ± 8.25	N.D.	0.12 ± 0.003
20 N.V.	N.D.	N.D.	N.D.	2.24 ± 0.36	15.93 ± 0.42	N.D.	N.D.	N.D.	N.D.	7.15 ± 1.95	N.D.	1.50 ± 0.01
20 V.	N.D.	N.D.	N.D.	2.21 ± 0.44	16.10 ± 1.73	N.D.	N.D.	N.D.	N.D.	4.81 ± 5.05	N.D.	1.44 ± 0.13
21 N.V.	N.D.	N.D.	N.D.	N.D.	23.09 ± 0.92	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
21 V.	N.D.	N.D.	N.D.	N.D.	22.10 ± 1.47	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
22 N.V.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	86.53 ± 4.32	N.D.	N.D.
22 V.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	80.27 ± 6.32	N.D.	N.D.
23 N.V.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.83 ± 1.29	N.D.	0.37 ± 0.10
23 V.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.50 ± 0.35	N.D.	0.32 ± 0.09
24 N.V.	N.D.	N.D.	N.D.	3.18 ± 0.28	56.80 ± 1.78	N.D.	N.D.	N.D.	N.D.	0.89 ± 0.13	N.D.	1.35 ± 0.08
24 V.	N.D.	N.D.	N.D.	3.26 ± 0.02	57.94 ± 2.3	N.D.	N.D.	N.D.	N.D.	0.97 ± 0.16	N.D.	1.38 ± 0.06

N.D. = Not Detected, V. = Vacuumed, N.V. = Not vacuumed.

Table 4
Comparison able of mask sample after immersion of saline solution concentrations in ($\mu g\ g^{-1}$).

Mask sample	Zn	Sb	Pb
19 N.V.	30.10	4.53	0.15
19 V.	26.36	5.16	0.12
19 N.V. saline	N.D.	N.D.	0.08
19 V. saline	N.D.	N.D.	0.07
20 N.V.	15.93	7.15	1.50
20 V.	16.07	4.81	1.44
20 N.V. saline	N.D.	N.D.	0.08
20 V. saline	N.D.	N.D.	0.07
21 N.V.	23.10	N.D.	N.D.
21 V.	22.10	N.D.	N.D.
21 N.V. saline	N.D.	N.D.	N.D.
21 V. saline	N.D.	N.D.	N.D.
22 N.V.	N.D.	86.50	N.D.
22 V.	N.D.	80.30	N.D.
22 N.V. saline	N.D.	1.01	N.D.
22 V. saline	N.D.	1.27	N.D.
23 N.V.	N.D.	1.83	0.37
23 V.	N.D.	1.50	0.32
23 N.V. saline	N.D.	0.08	0.08
23 V. saline	N.D.	0.11	0.11
24 N.V.	56.80	0.97	1.38
24 V.	57.94	0.89	1.35
24 N.V. saline	N.D.	N.D.	0.10
24 V. saline	N.D.	N.D.	0.09

N.D. = Not Detected, V. = Vacuumed, N.V. = Not vacuumed.

whereas for the two masks for sample #23 the values were 4% and 7% respectively.

The percentages of leaching for Pb were much higher in all masks that contained Pb. Specifically, in the two different masks for sample #19, 53% of Pb was transferred to the leachate in the non-vacuumed and 58% in the vacuumed mask. For samples #20 and #23 the percentages of Pb transferred were 5% in both the non-vacuumed and vacuumed masks, and 22%, 34% in the non-vacuumed and vacuumed masks respectively. Considering the short time of exposure (6 h) to the saline solution, the values of leachable Pb were of considerable magnitude as half the original Pb amount in masks #19 leached out. This is indicative of how trace elements in a mask may affect a mask user through their saliva. The exposure could occur in people who may use contaminated masks for extensive periods of time or for children who may chew the mask material. It is also important to point out that unlike our saline solution, human saliva contains a multitude of enzymes that could enhance metal leaching. Further studies should investigate varying the time and saline concentration to see if this variation affects the amount of Pb that comes out of the face masks. Concentrations from masks that have the "Saline" identifier refer to heavy metals and metalloids from the saline leachate. As it is noted, ICP-MS of water leachates from disposable face masks were also reported in the recent study by Sullivan et al. (Sullivan et al., 2021). Table 5 presents the highest levels of heavy metals and metalloids determined in the present study ($d \approx 1.04$ g mL^{-1}) in comparison to the aforementioned study.

As shown, the levels of Pb and Sb found in the present study are higher than those measured by the Sullivan et al. study, in which the samples were leached for a much longer time (24 h). It should be noted Sullivan et al. have not carried out a total acid digestion of mask materials but only analyzed the metals of a water leachate solution, whereas herein total digestion as well as analysis in the saline leachate solution were performed. An interesting point from comparing the data is that the saline leachate solution of our study leached out 16 times more Pb, and about 3 times more Sb than the water leachate.

4. Conclusions

As a first nonpharmacological line of defense against SARS COVID-19, the World Health Organization, the C.D.C. in U.S., and other health organizations around the globe have recommended or at times have made it mandatory, that the public conducts social activities while wearing face masks. This practice is indeed historically documented to be highly effective and has helped people tremendously in reducing the spread of the viruses, including coronavirus, during the current pandemic. While the function and utility of masks is indisputable, as the present study indicates, there is a pressing need that face masks, which are widely available in the marketplace and come from many manufacturers, pass strict quality control and quality assurance tests. This is especially important for the ones designated for children, which should be free of toxic substances. As present study reveals, presently, most masks contain trace elements below the detection limit but there exist a few masks with detectable values of trace elements. In addition, the saliva experiments demonstrate there is a high possibility that trace elements can leach out of a mask that contains them. Specifically, in one of the conducted experiments, Pb leached out close to 60% after a 6-h exposure to a saline solution. While our study marks the beginning of the investigation of contaminants in masks, we believe that future studies are necessary to expand its scope with the analysis of different contaminants.

Table 5
Reported highest levels of heavy metals and metalloids in disposable face masks.

Description	Pb ($\mu g\ L^{-1}$)	Sb ($\mu g\ L^{-1}$)	Reference
Total digestion	1.38E+04	9.38E+04	This study
Saline leachate	1.1E+02	1.32E+03	This study
Water leachate	6.79E+00	3.93E+02	Sullivan et al. (Sullivan et al., 2021)

CRediT authorship contribution statement

Derek D. Bussan: Methodology, Funding acquisition, Investigation.
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George Bartzas: Methodology, Formal Analysis, Writing - Review & Editing.
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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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